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Compound Formation, Solubility, and Ionization in Fused Salt Mixtures

II. Compound Formation between Antimony and Aluminium Chlorides and other Metallic Chlorides.

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By

HENRY KEPPELE MILLER, Jr., B.S., M.A.

DISSERTATION

Submitted in Partial Fulfillment of the Requirements for the
Degree of Doctor of Philosophy in the Faculty of
Pure Science of Columbia University in the
City of New York

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ACKNOWLEDGMENT.

THE author wishes to express to Professor James Kendall, at whose suggestion this investigation was undertaken, his sincere gratitude for his constant advice and kindly interest throughout the course of the work.

The author is also glad to take this opportunity to acknowledge with thanks the interest and co-operation of the other members of the Chemistry Department of Columbia University.

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ABSTRACT OF DISSERTATION

1. What was attempted?

2. In how far were the attempts successful?

3. What contribution actually new to the science of chemistry has been made?

1. The attempt was made to demonstrate the applicability of rules previously formulated governing the variation of addition compound formation to fused salt mixtures. Systems of the type RCl-$R'Cl$ were chosen, the particular systems studied being antimony trichloride—metallic chloride, and aluminium chloride—metallic chloride.

2. (a) It has been shown that compound formation and solubility increase with the diversity between R and R'. This diversity, measured by the relative positions of R and R' in the electromotive series, is the main factor, but there are additional points which must be taken into account.

(b) It has been shown that of these additional factors the most important is valence.

(c) The stability of compounds is greatest when the temperature of fusion is low.

(d) Large differences in internal pressures tend toward the formation of two liquid layers.

3. (a) The initial steps in the formulation of a generalized theory of ionization have received additional experimental confirmation.

(b) Twenty-eight new systems have been investigated by the freezing point method.

(c) Seventeen compounds have been isolated for the first time.

(d) Two new crystalline modifications of antimony trichloride have been discovered.

INTRODUCTION

In the early[1] articles of this series, from studies of the freezing point curves of systems consisting of various pairs of organic compounds, the theory was advanced that the extent of compound formation, as well as the complexity and stability of the compounds, depends essentially upon the difference in chemical character of the two components. This diversity factor is determined by the position of the elements in the electrode potential series. The greater the difference, in general, the greater will be the compound formation. As the work was continued[2] it was pointed out that solubility increased with compound formation and that compound formation and ionization proceeded in parallel. Additional factors influencing solubility, compound formation and ionization were noted and discussed to some extent.

In the present paper we will discuss the effect of polarity, internal pressure, atomic diameter, temperature, valence and unsaturation upon the compounds formed and their stability, in systems of fused salts. Systems of the type RX-HX[3], HX-HOH[4], ROH-HOH[4] and HX-HX′-HOH[5] have already been discussed with encouraging results, but before the generalizations there deduced could be applied to the system RX-HOH—one of the ultimate goals of this series—more investigation had to be undertaken. Consequently it was decided to see if the same rules held for fused salt mixtures, comparing R and R′ while keeping the negative element constant, as for R and H in the previous work. In order to show the effect of the factors outlined above it was desired to use a salt as solvent which would have a low melting point, which would be removed from H in the E.M.F. series, which would have a low internal pressure and which was not uniunivalent. Aluminium chloride, aluminium bromide and antimony trichloride were all satisfactory

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[1] For résumé see Kendall, Booge and Andrews, J.A.C.S. *39* 2304 (1917) Kendall and Booge, ibid *39* 2323 (1917).

[2] Kendall and Gross, ibid *43* 1416 (1921); Kendall and Davidson, ibid *43* 979; Kendall and Adler, ibid *43* 1470; Kendall, Davidson and Adler, ibid *43* 1481 and 1846.

[3] Kendall and Landon, ibid *42* 2131 (1920); Kendall and Davidson, loc. cit.; Kendall and Adler, loc. cit.

[4] Kendall, Adler and Davidson, loc. cit.

[5] Kendall and Andrews, J.A.C.S. *43* 1545 (1921).

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though only slightly polar.[1] Systems in these solvents have been simultaneously investigated—the bromides by Crittenden[2] and the chlorides in the present investigation. The solvent action of aluminium chloride will be compared with that of aluminium bromide and antimony trichloride. These systems will also be compared with previous work in which hydrogen was the reference element. In so doing it is hoped to extend the rules already formulated to systems of fused salts and to discuss more fully the varying factors, especially valence and unsaturation.

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[1] This was at first thought to be unfavorable, for Lewis has shown J.A.C.S. *35* 1448 (1913) and *38* 762 (1916), that polar compounds should form more molecular complexes than non-polar. However, slightly polar compounds become more polar in the presence of more strongly polar compounds and the compounds formed are sufficient.

[2] Columbia University Dissertation, 1922.

TABLE I

NH_4	Li	Cs	Rb	K	Ba	Na	Sr	Ca	Mg	Mn^{++}	Zn	Cd	Tl^{+}	Pb^{++}	Sn^{++}	Fe^{+++}	Bi	Cu^{++}	Ag	Hg^{++}
	Ea										1-2a	1-2 1-1a	insol a	insol a		1-1a		Ea		
		1-1l 1-2l Sb	Eb	Eb		Sb		Si	Si				Ei	Ef				1-2h Si	Si	
			Sb	Sb		Eb							Si					1-2i 3-2i	1-1h	
				Se		Eb							Si					1-2i 3-2i	Ei	
						Sj		1-1g	1-1 2-1g			Eg	Si	4-1 2-1c 1-2				2-1h	Eb	
						Ed	Si	1-1h Si		2-1i	1-1h	Ei	Eh	Si						
								4-1g	1-1g			Eg	Ei					Si	Si	
								Sik	Ei	Ei	1-1h	Ei	1-1h	Si						
									Sg	Si	Eg	Sig	1-1h	Ei	Eg					
										Si	Eg	Sg	2-1h	Eg	Eg			Eg	Eg	
											Ei	Sl		Ei	Ei					
												Ee	1-2h 2-1h	Ee	Ee	Se	Se 2layers	Se		Ei 2layers
													1-1h	Ee	Ee	Ee		Se		
														1-2h 3-1	1-1h 3-1			2-1 h i	3-2 i	4-1i 1-1i
															Sel	Ee	Ee	Ee		
																		Ee		
																	Ee	1-1e		
																		Ee		

a. K. Hachmeister, Z.a.C., *109*, 145 (1919).
b. Zemczuzny, Z.a.C., *57*, 267 (1908); *65*, 403 (1910).
c. Lorenz and Ruckstall, Z.a.C., *51*, 70 (1906).
d. LeChatelier, Comptes Rendus *118*, 800 (1894).
e. Herrman, Z.a.C., *71*, 257 (1911).
f. Treis, Diss. Berlin, 1914.
g. Menge, Z.a.C., *72*, 162 (1911).
h. Liebish and Korreng, Spitzb. preuss. Akad. Wissenschaften, 1914, 192.
i. Sandonnini, Gazz. chim. ital. 44 I 290.
j. Kumakow and Zemczuzny, Z.a.C., *52*, 186 (1907).
k. Schaefer, Neues Jahrb. Min. Geol., 1914, I, 290.
l. Korreng, Z.a.C., *91*, 194 (1915).

PREVIOUS WORK ON BINARY SYSTEMS OF CHLORIDES

A considerable quantity of work has been done in determining binary systems of fused chlorides, but the investigators differ in their results and the pairs chosen are for the most part the very ones which from the present theory should not give many compounds. It is conspicuous that monovalent chlorides have been run against monovalent chlorides, divalent against divalent, and with the higher valences and systems of mixed valence we have but a few isolated examples. One of the investigators[1] has remarked about the scarcity of compounds, but no theoretical conclusions relative to compound formation have been derived. All the freezing point work on binary systems of fused chlorides reported in the literature has been tabulated in Table I. In the table compounds are represented by numbers, the first figure representing the proportion of chloride of the element in the left-hand column—$SnCl_2$, $2AlCl_3$ would be a 1-2 compound. The small letters refer to the investigator. Solid solution is denoted by S and a simple eutectic by E.

The literature is full of other binary compounds of chlorides, but these have for the most part been precipitated from hydrochloric acid solution or crystallized from some organic solvent. As the solvent in most cases influences the compounds formed[2], these have been omitted from consideration except in the case of the compounds claimed for the reference substances of this investigation. From the table it is clear that the general premises of the theory hold for the system RCl-R′Cl. It seems best to delay a discussion of the table until after the experimental work of this investigation has been examined in detail and then to give a summary of the entire field of binary systems of fused chlorides.

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[1] Sandonnini loc. cit.

[2] The molecular proportions of a compound as hydrate, alcoholate, acetonate, etc., vary in most cases.

EXPERIMENTAL PROCEDURE

In the present work $SbCl_3$ was used as solvent for the chlorides of NH_4, Li, K, Na, Ba, Al, $Sn^{\cdot\cdot}$, $Sn^{\cdot\cdot\cdot\cdot}$, Cu^{+}, Hg^{+}, $Hg^{\cdot\cdot}$, and Ag; and $AlCl_3$ as solvent for the above and in addition for the chlorides of $Cr^{\cdot\cdot}$, $Cr^{\cdot\cdot\cdot\cdot}$, $Mn^{\cdot\cdot}$, and Tl^{+}. The solutions were studied by the freezing point method[1]. Due to the hygroscopic nature of the solvents it was necessary to use closed tubes throughout the investigation and to limit the experimental work to clear, cold, dry days. It was found advantageous to abandon the method used heretofore in this series of researches of sealing a glass rod, as a handle, to a small bulb containing the weighed sample. Instead, a small bulb was blown on the end of a glass tube. The tube was weighed, the less hygroscopic chloride was introduced and the tube weighed again. The other chloride was then quickly introduced and the tube sealed, allowing as little air space as practicable. The tube was now thoroughly cleaned, dried, and weighed. From these data the molecular percentages of the two components could be calculated. After a little practice the quantities could be judged so as to obtain a representative set of tubes with little difficulty. Where indications of compound formation were apparent the spacing between tubes was lessened so as to emphasize as much as practicable the breaks in the curve. Both for the facility of glass blowing and to withstand the pressures created it was found expedient to use Pyrex glass throughout the investigation. In previous work[2] it has been shown that by agitating the tube in the bath and noting the disappearance of the last crystals the melt-points are reproducible within the accuracy of the investigation provided the temperature of the bath is raised at a rate of not more than 0.2° per minute.

The following substances were used as baths:

CO_2(solid)—alcohol	—40° to —20°
HNO_3 (fuming)—ice	—20° to —10°
Salt—ice	—10° to room
Water	room to +100°
30% $(NH_4)_2SO_4$-70% H_2SO_4	+100° to +200°
KNO_3-$NaNO_3$-$Ca(NO_3)_2$[3]	+200° to +300°
KNO_3-$NaNO_3$	+300° to +600°

Four mercury thermometers were used, covering ranges from

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[1] For an account of this method see earlier papers of this series.

[2] Adler, Columbia University Dissertation, 1920.

[3] Menzies and Nutt, J.A.C.S. *33* 1366 (1912).

—50° to +25°, +5° to +105°, +90° to +205° and +195° to 300° respectively, and graduated in tenths of a degree. They were standardized by comparison with a platinum resistance thermometer[1], which was checked against the freezing and boiling of water and the boiling of sulphur, according to the specifications of the Bureau of Standards[2]. The tubes always being immersed to the same depth, the conditions of experimentation and calibration were the same and stem corrections did not have to be applied. For temperatures above 300°, a base metal thermocouple[3] was used with a low resistance galvanometer, reading temperature directly, which was likewise standardized against the platinum resistance thermometer.

Every freezing point was determined at least twice. The precision of measurement varied with the temperature and with the slope of the curve, so that it is difficult to give any definite probable error values. The melting points given are probably accurate within the values given below, and are reproducible within much more narrow limits.

Temperature	—40°	to	—10°	error	0.5°	to	1.0°
	—10		+100		0.3		0.5
	+100		200		0.5		1.0
	200		300		1.0		1.5
	300		600		2.0		5.0

For very steep portions of the curve the above errors may be somewhat exceeded.

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[1] The delta of this thermometer was 1.63, which is sufficiently low for all but the most precise work.

[2] Reprint No. 124.

[3] Portable Pyod.

EXPERIMENTAL DATA

Antimony trichloride was made by the method of Hensgen,[1] by passing chlorine over lumps of metallic antimony. It was found efficacious to make the pentachloride first and then to reduce with powdered antimony to the trichloride. By fractional distillation a clear distillate was obtained, boiling at 232-234°. This product was then purified by sublimation at 100°, and the crystals were shaken into weighing bottles and kept over P_2O_5 in vacuum desiccators. The product consisted of pure white glistening crystals melting sharply at 73°.4 ±0.2

Aluminium chloride was prepared by passing washed and dried hydrogen chloride over hot C.P. aluminium in the form of a coarse powder, which had been thoroughly washed in alcohol to remove all traces of oil. All traces of moisture were driven from the apparatus and the product was sublimed directly into a weighing bottle. This aluminium chloride was of a good color, showing only the very slightest trace of pale yellow, and melted sharply at 190°.2± 0.2.

ANALYSES

Due to the hygroscopic nature of the substances and the high temperatures involved it was impracticable to make analyses, but from the shape of the curves there is no difficulty in determining the compounds formed, except in the cases indicated by interrogation points.

LIMIT OF CURVES

It was found inadvisable to carry tubes with aluminium chloride much above 300° as the large increase in volume showed that the critical temperature was fast being reached and annoying explosions, due to the increased pressure, were likely to ensue. Similarly for the systems containing a two layer region the temperature of coalescence was not determined.

(1) SYSTEM $SbCl_3$-NH_4Cl. See also curve D, Fig. 1.

The ammonium chloride was "chemically pure," recrystallized from distilled water and dried to constant weight.

The compounds $NH_4Cl,SbCl_3$[2];$2NH_4Cl,SbCl_3$[2];$3NH_4Cl,SbCl_3$[3] have been reported previously.

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[1] Rec. Trav. Chim. Pays-Bas, 9 301 (1890).

[2] Wheeler, Am. J. Sci. (3) 46, 269. Wells and Metzger ibid (4) 11, 451. Wells, Am. C. J. 26, 389 (1901).

[3] Fehlings Handwörth.

The freezing point results of the present work are given below. T indicates temperature of disappearance of solid phase.

(a) Solid phase $SbCl_3$ (alpha)

%NH_4Cl	0.00	2.07	2.60	4.38	6.56	7.49	8.17
T.	73.4	71.3	70.8	69.7	68.1	67.5	66.5

*(b) Solid phase $SbCl_3$ (beta)

%NH_4Cl	7.28	7.49	8.92	9.89
T.	68.2	68.0	66.6	65.7

*(c) Solid phase $SbCl_3$ (gamma)

%NH_4Cl	12.52	14.11	18.10
T.	64.4	63.1	59.5

(d) Solid phase $NH_4Cl,SbCl_3$

%NH_4Cl	19.81	22.92	25.53	27.63	31.28	34.72	36.17
T.	70.0	89.2	104.1	110.6	123.1	134.8	139.7

*(e) Solid phase $3NH_4Cl,2SbCl_3$

%NH_4Cl	37.22	42.18	43.20	47.39	55.28	58.89	61.69
T.	157.4	217.8	228.6	253.5	284.3	290.5	289.5

(f) Solid phase NH_4Cl

%NH_4Cl	63.47	64.62	66.70	68.66	72.25	81.28	85.89
T.	289.5	296.8	305.8	318.0	338.5	392.	418.

The curve was not carried further for fear of the pressure breaking the tubes, but upon extrapolation the curve shows the melting point of ammonium chloride to be above 500°, which compares favorably with the reports in the literature.[1] The equimolecular compound reported is confirmed, but no indications of the other two could be obtained.[2] The compound $3NH_4Cl,2SbCl_3$ melting at 291° is reported for the first time. Three crystalline modifications of antimony trichloride are also first noted here and later are confirmed in the system $SbCl_3$-KCl. The transition temperatures are 69°.5 and 65°.0. Three crystalline modifications have been previously reported[3] for antimony triiodide.

(2) SYSTEM $AlCl_3$-NH_4Cl. See also curve B, Fig. II.

The same ammonium chloride was used as above.

The only compound reported[4] is $NH_4Cl,AlCl_3$.

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* Reported for the first time.

[1] Langmuir, J.A.C.S., *42*, 281 (1920).

[2] It will be noted that they were reported in aqueous solution and it is not suprising that they were not obtained in the present work.

[3] Abegg, Handbuch der Anorganischen Chemie, III, 3, 590.

[4] Baud, Ann. Chim. Pnys., 1904 (viii) *1*, 8. The author heats his two chlorides together in varying proportions and sublimes off the excess aluminium chloride. He then calls what remains a compound of the composition given by analysis.

The results of the present work are given below.

*(a) Solid phase "Two layer compound" $xNH_4Cl,yAlCl_3$

$\%NH_4Cl$	0.2	20.61	23.80	28.55	31.91
T.	192.2	192.3	186.6	171.8	157.9

(b) Two layer region

$\%NH_4Cl$	0.84	1.27	7.80	14.52	16.13
T.	192.5				192.5

(c) Solid phase $NH_4Cl,AlCl_3$

$\%NH_4Cl$	33.18	36.86	38.25	43.54	49.14	53.06	56.76	58.45
T.	173.4	229.4	239.7	274.1	301.2	287.2	266.1	257.1

(d) Solid phase NH_4Cl (?)

$\%NH_4Cl$	61.00	65.10	72.77
T.	284.3	357.	did not dissolve at 370° for 6 hrs.

At 70% the curve was rising rapidly, presumably separating out ammonium chloride. The equimolecular compound reported is confirmed, and in addition we report an unstable compound of undetermined composition which breaks up into two liquid layers.[1] It was impracticable to make a tube that would give $AlCl_3$ as the solid phase since one containing as little as 0.2% NH_4Cl gave the compound $xNH_4Cl,yAlCl_3$. There is without doubt a short eutectic and then a sudden rise in the curve. Similar behavior will be noted often in this work and in that on the fused bromides.[2]

(3) SYSTEM $SbCl_3$-LiCl.

C.P. lithium chloride was dissolved in distilled water and lithium carbonate was precipitated by ammonium carbonate. This product was decomposed by hydrochloric acid, the solution was evaporated and the first crop of crystals were carefully dried to constant weight.

It was not possible to obtain a solubility curve for this system. A mixture containing 0.6% LiCl was to all appearances insoluble after being kept at a temperature of 300° for 6 hours.

(4) SYSTEM $AlCl_3$-LiCl. See also curve D, Fig. II.

The same lithium chloride was used as above.

(a) Solid phase $AlCl_3$

%LiCl	0.00	6.61	17.16	20.11	29.58	38.40	40.08
T.	190.2	190.0	187.9	186.4	171.4	125.6	114.4

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[1] This behavior is rather rare. See Roozeboom, Heterogene Gleichgewichte, II, 2, 168.

[2] Crittenden, loc. cit.

*(b) Solid phase $LiCl$-$AlCl_3$

%LiCl	43.21	45.83	47.42	49.60
T.	117.8	132.8	139.9	143.0

(c) Solid phase LiCl (?)

%LiCl	49.60	50.54	51.08
T.	170.4	338.5	did not dissolve.

At 51% the curve was rising rapidly, presumably to the fusion point of pure lithium chloride. The results plainly show the existence of an equimolecular compound reported here for the first time, unstable at its maximum.

(5) SYSTEM $SbCl_3$-NaCl.

The sodium chloride was C.P., recrystallized and dried to constant weight.

The compound $SbCl_3$,3NaCl has been reported.[1]

It was found impossible to run this system, as a mixture containing 0.53% NaCl showed no signs of dissolving at 300° for 6 hours. The compound reported was obtained from an aqueous solution and is not comparable with the present work.

(6) SYSTEM $AlCl_3$-NaCl. See also curve C, Fig. II.

The following compounds have been reported:[2] NaCl,$AlCl_3$; 3NaCl,2$AlCl_3$; 3NaCl,$AlCl_3$.

(a) Solid phase Two layer compound, xNaCl,y$AlCl_3$

%NaCl	20.09	22.15	26.14	30.63	33.88	37.32
T.	192.0	190.0	182.0	169.4	151.3	130.2

*(b) Two layer region

%NaCl	0.22	1.39	10.80	17.29
T.	193.5			193.5

(c) Solid phase NaCl,$AlCl_3$

%NaCl	41.07	44.79	47.62	48.28
T.	123.6	140.7	147.9	151.9

(d) Solid phase NaCl (?)

%NaCl	48.44	49.51	51.75
T.	153.7	320.5	did not dissolve.

At 51% the curve was rising rapidly. Baud's equimolecular compound is confirmed, while the other two are beyond the range of this work.

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[1] Wheeler and Wells, loc. cit.

[2] Baud, loc. cit.

(7) SYSTEM $SbCl_3$-KCl. See also curve C, Fig. I.

The potassium chloride was C.P., recrystallized and dried to constant weight.

Three compounds have been previously reported: $2KCl,SbCl_3$[1]; $7KCl,3SbCl_3$[1]; $3KCl,SbCl_3$.[2]

(a) Solid phase $SbCl_3$ (alpha)

%KCl	0.00	0.74	1.60	4.42	5.05	5.51	6.41
T.	73.4	72.4	71.8	69.8	69.2	68.9	68.3

(b) Solid phase $SbCl_3$ (beta)

%KCl	8.66	11.81	12.33	14.96	18.05
T.	67.4	64.6	64.1	62.0	59.2

(c) Solid phase $SbCl_3$ (gamma)

%KCl	18.96	22.25	23.78
T.	60.3	58.0	57.0

*(d) Solid phase $KCl,SbCl_3$

%KCl	28.00	29.52	32.57	36.18	37.89
T.	69.8	79.7	94.8	109.4	113.3

*(e) Solid phase $3KCl,2SbCl_3$

%KCl	39.25	41.03	46.84	48.80	54.75
T.	118.3	162.5	250.5	277.1	320.0

(f) Solid phase KCl

%KCl	58.50	61.75	68.71
T.	360.	433.5	533.

Throughout this series it has been noted that curves with KCl and NH_4Cl are similar and it was thought unnecessary to carry the curve above 550°. An equimolecular compound, cut off before reaching its maximum, as in the case of NH_4Cl, and a second compound, cut off at 58%, most probably $3KCl,2SbCl_3$, corresponding to the ammonium chloride curve, are reported for the first time. The other compounds previously reported are not confirmed. The three modifications of antimony trichloride noticed in the system $SbCl_3$-NH_4Cl are again evident.

(8) SYSTEM $AlCl_3$-KCl. Curve is similar to C, Fig. II.

The compounds reported[3] by previous workers are: KCl, $AlCl_3$; $3KCl,2AlCl_3$; $3KCl,AlCl_3$; $2KCl,AlCl_3$.

(a) Solid phase, Two layer compound, $xKCl,yAlCl_3$

%KCl	19.04	23.04	27.01	31.22
T.	192.5	187.4	177.2	162.1

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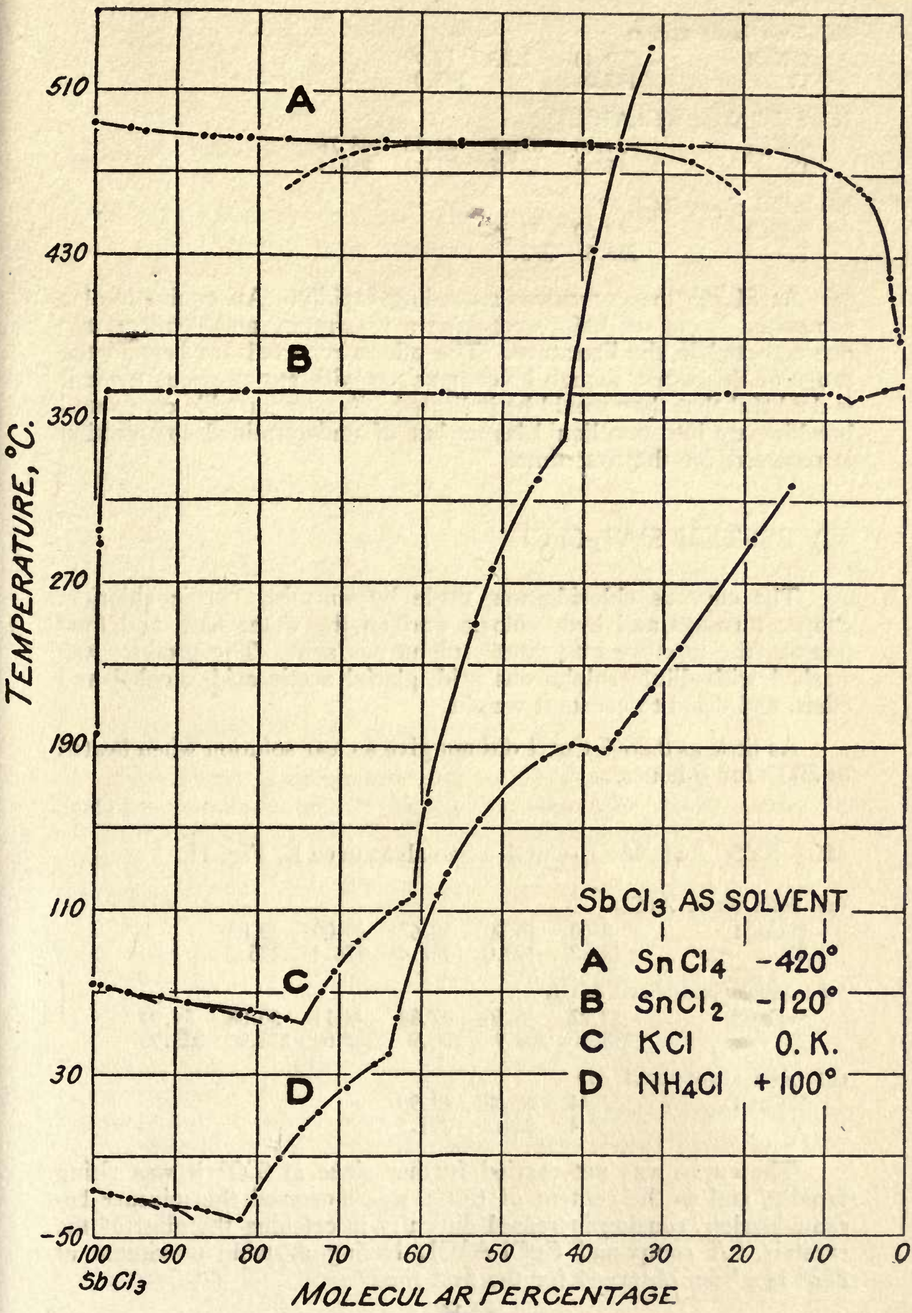
[1] Wells and Wheeler, loc. cit.

[2] Fehlings Handwörtb.

[3] Baud, loc. cit.



TEMPERATURE, °C.
510
430
350
270
190
110
30
-50
100
90
80
70
60
50
40
30
20
10
0
$SbCl_3$
MOLECULAR PERCENTAGE
A
B
C
D
$SbCl_3$ AS SOLVENT
A $SnCl_4$ -420°
B $SnCl_2$ -120°
C KCl 0. K.
D NH_4Cl +100°

Fig. I.

(b) Two layer region

%KCl	0.40	1.83	16.99
T.	193.0		193.0

(c) Solid phase $KCl,AlCl_3$

%KCl	34.48	37.47	42.95	48.78
T.	158.4	178.7	213.1	248.4

(d) Solid phase KCl (?)

%KCl	49.50	51.52
T.	255.5	375.

At 51.5% the curve was ascending rapidly. An equimolecular compound is cut off before reaching a maximum, and confirms the one reported in the literature. The others reported are beyond the range of this work, though by comparison with our previous work it is doubtful that they would be indicated. A new unstable compound breaking up into two liquid layers but of undetermined composition is reported for the first time.

(9) SYSTEM $SbCl_3$-CuCl.

The cuprous chloride was made by warming cupric chloride, copper turnings and hydrochloric acid on the water bath and then pouring the mixture into dilute sulphurous acid. The product was washed with dilute sulphurous acid, glacial acetic acid, alcohol and ether, and dried to constant weight.

As little as 0.26% CuCl did not give a clear solution when heated to 300° for 6 hours.

(10) SYSTEM $AlCl_3$-CuCl. See also curve E, Fig. II.

(a) Solid phase $AlCl_3$

%CuCl	0.00	10.50	19.67	29.00	30.83
T.	190.2	190.0	187.4	178.3	175.3

*(b) Solid phase $CuCl,AlCl_3$

%CuCl	32.22	40.56	47.88	48.11	50.88	54.00
T.	178.3	209.9	230.9	232.6	231.9	225.9

(c) Solid phase CuCl (?)

%CuCl	57.44	60.08	61.98
T.	227.4	252.5	291.5

The curve was not carried further since at 300° it was rising rapidly, and as the content of CuCl was increased the mixture became blacker, causing increased difficulty in catching the glint of the crystals. A compound $CuCl,AlCl_3$ having a stable maximum at 232° has been observed for the first time.

(11) SYSTEM $SbCl_3$-$AgCl$.

Silver chloride was precipitated from U.S.P. $AgNO_3$ and hydrochloric acid, thoroughly washed and dried to constant weight.

The tubes were still turbid after 6 hours at 300° with as little as 0.18% $AgNO_3$.

(12) SYSTEM $AlCl_3$-$AgCl$. Curve is similar to C, Fig. II.

*(a) Solid phase Two layer compound $xAgCl,yAlCl_3$

%AgCl	0.38	20.12	26.48	32.59	33.37	38.02	39.75
T.	191.2	190.1	184.5	161.5	156.0	136.8	121.9

(b) Two layer region

%AgCl	2.10	6.64	16.38
T.	192.9		192.9

*(c) Solid phase $AgCl,AlCl_3$

%AgCl	39.95	43.60	46.98
T.	122.2	138.9	147.5

(d) Solid phase AgCl (?)

%AgCl	47.90	49.10	50.85
T.	175.4	285.3	378.

At 50% the curve was rising very rapidly and it is probably safe to assume that AgCl is the solid phase separating. Two unstable compounds are here reported for the first time, one, of equimolecular composition, cut off a little beyond 47%, and the other, of undetermined composition, breaking up into two liquid layers.

(13) SYSTEM $AlCl_3$-$MgCl_2$.

C.P. magnesium chloride was recrystallized as the double ammonium salt, and the ammonium chloride was driven off by gentle heating until no test for the ammonium ion was evident.

(a) Solid phase $AlCl_3$

%$MgCl_2$	0.00	9.52	12.42	15.43
T.	190.2	188.6	187.4	186.4

(b) Solid phase $MgCl_2,2AlCl_3$ (?)

%$MgCl_2$	17.93	22.14	27.51	29.13	30.90
T.	188.0	207.6	224.2	227.4	did not dissolve

Tubes containing 30.9% magnesium chloride, and higher, would not give a clear solution even when heated to 350° for 6 hours. The curve appears to be bending, so that $MgCl_2$ is apparently not separating, and from a comparison with the other curves it seems altogether likely that the solid phase is the compound $MgCl_2,2AlCl_3$.

(14) SYSTEM $SbCl_3$-$BaCl_2$.

Anhydrous barium chloride was obtained by carefully fusing the recrystallized C.P. dihydrate.

By heating to 300° for 6 hours it was impossible to obtain a clear solution with a tube containing 0.4% $BaCl_2$.

(15) SYSTEM $AlCl_3$-$BaCl_2$.

The compound $BaCl_2,2AlCl_3$ has previously been reported.[1]

(a) Two layer region

%$BaCl_2$	2.08	7.35	11.23
T.	191.5		191.5

(b) Solid phase $BaCl_2,2AlCl_3$ (?)

%$BaCl_2$	14.00	20.06	22.83	27.11	30.43
T.	192.5	198.8	209.4	255.5	did not dissolve

Here we have a two liquid layer region of the more common type, i.e., it is not formed by the decomposition of an unstable compound. The curve rises quite rapidly and a mixture of 30% $BaCl_2$ will not give a clear solution. However, from the slope, the compound $BaCl_2,2AlCl_3$ is possible, and from a comparison with our other curves is quite probable, which fact would confirm the compound reported.

(16) SYSTEM $SbCl_3$-HgCl.

The mercurous chloride was prepared in the usual manner by precipitation from a saturated solution of mercurous nitrate, containing excess mercury and nitric acid, with hydrochloric acid. The product was thoroughly washed and dried to constant weight.

All tubes containing more than 2% HgCl were insoluble under the conditions of experimentation. Tubes containing 0.42% and 0.61% melted at 74° and 235° respectively and show how very rapidly the curve rises.

(17) SYSTEM $AlCl_3$-HgCl.

The tubes showed a great tendency to explode and even those containing a low percentage of HgCl blackened considerably. Consequently work upon the system was abandoned.

(18) SYSTEM $SbCl_3$-$HgCl_2$.

The mercuric chloride was recrystallized from distilled water and dried to constant weight.

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[1] Baud, loc. cit.

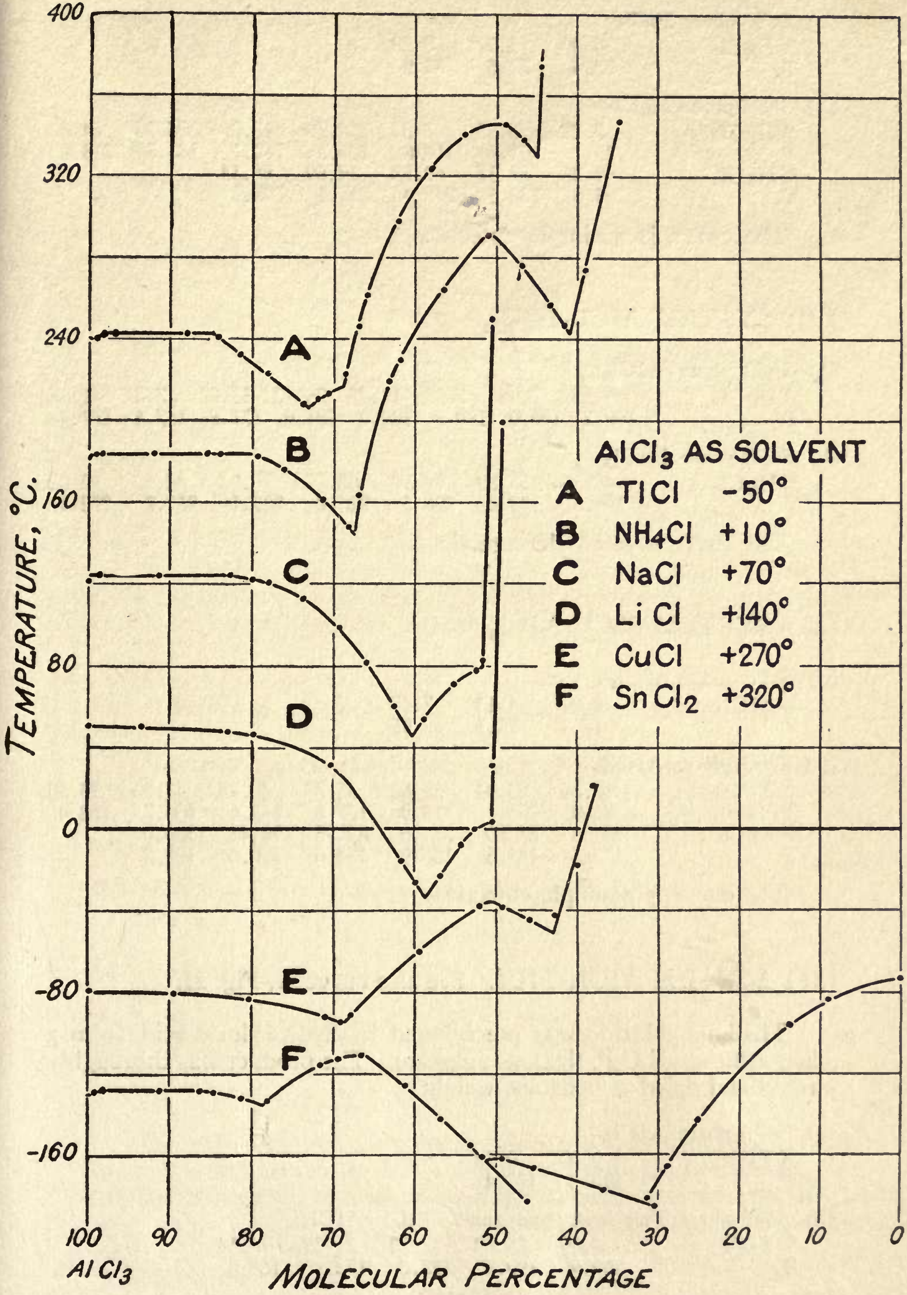
400
320
240
160
80
0
-80
-160
Temperature, °C.
100
90
80
70
60
50
40
30
20
10
0
Al Cl$_3$
Molecular Percentage
A
B
C
D
E
F
AlCl$_3$ AS SOLVENT
A TlCl -50°
B NH$_4$Cl +10°
C NaCl +70°
D Li Cl +140°
E CuCl +270°
F SnCl$_2$ +320°

Fig. II.

(a) Solid phase $SbCl_3$

%$HgCl_2$	0.00	1.97	3.28
T.	73.4	72.6	71.9

(b) Solid phase $HgCl_2$

%$HgCl_2$	5.22	6.55	8.35	9.79	13.06	25.38	44.33
T.	85.4	101.7	114.8	126.3	142.1	183.5	218.8
%$HgCl_2$	49.26	58.37	69.58	79.60	86.14		
T.	225.6	234.5	246.4	257.1	264.2		

The curve is a simple eutectic.

(19) SYSTEM $AlCl_3$-$HgCl_2$.

(a) Solid phase $AlCl_3$

%$HgCl_2$	0.00	2.96	7.67	18.47	26.42	32.78	37.37	41.37
T.	190.2	190.0	189.7	189.0	184.6	177.5	167.5	157.4

(b) Solid phase $HgCl_2$

%$HgCl_2$	48.16	55.88	58.10	63.18	70.92	82.60	90.02
T.	151.3	192.0	200.5	216.2	238.1	259.7	272.1

The curve is a simple eutectic.

(20) SYSTEM $SbCl_3$-$AlCl_3$.

(a) Solid phase $SbCl_3$

%$AlCl_3$	0.00	4.13	7.47
T.	73.4	71.1	69.95

(b) Solid phase $AlCl_3$

%$AlCl_3$	15.24	23.04	25.63	35.78	40.48	47.80	53.26
T.	83.0	106.1	112.9	137.3	147.6	160.7	168.4
%$AlCl_3$	58.58	67.80	78.06	82.95	96.42	100.0	
T.	173.6	181.6	186.9	188.6	190.0	190.2	

The curve is a simple eutectic.

(21) SYSTEM $AlCl_3$-$TlCl$. See also curve A, Fig. II.

Thallous chloride was precipitated by hydrochloric acid from a dilute solution of C.P. thallous sulphate. The product was thoroughly washed and dried to constant weight.

(a) Solid phase $AlCl_3$

%$TlCl$	0.00	0.52
T.	190.2	189.4

(b) Solid phase Two layer compound $xTlCl,yAlCl_3$

%$TlCl$	0.90	15.62	18.73	21.85	26.14
T.	189.9	190.2	182.3	172.8	158.8

(c) Two liquid layer region

%T1C1	1.76	3.11	12.10
T.	192.0		192.0

*(d) Solid phase $T1C1,2A1C1_3$

%T1C1	28.22	29.24
T.	160.5	162.9

*(e) Solid phase $T1C1,A1C1_3$

%T1C1	31.44	33.06	34.19	37.90	42.06	46.20	51.17	53.46
T.	172.6	196.6	211.4	248.1	174.1	290.0	295.5	288.1

(f) Solid phase T1C1 (?)

%T1C1	55.52	56.48
T.	325.	did not dissolve

The melting points of the tubes containing a large percentage of T1C1 were very difficult to obtain because of a slight opalescence. It has been previously noted[1] that T1C1 will not give an optically clear solution and this turbidity is exceedingly hard to distinguish from the last few crystals. An equimolecular compound having a stable maximum at 296° and two unstable compounds are here reported for the first time. One of these latter is cut off at 30% and is undoubtedly $T1C1,2A1C1_3$; the other is of undetermined composition and decomposes into two liquid layers. This is the first curve in which the eutectic on the aluminium chloride side of the unstable two layer compound has been determined.

(22) SYSTEM $SbC1_3$-$SnC1_2$. See also curve B, Fig. I.

The stannous chloride was prepared by digesting tin with hydrochloric acid. The product was redistilled and then fused in the presence of as little air as possible. Only the center portion of the fused mass melting at 246.8 was used.

*(a) Solid phase Two layer compound $xSnC1_2ySbC1_3$

$\%SnC1_2$	0.10	0.71	0.85	91.75	92.70
T.	74.9	169.0	174.9	242.1	240.7

(b) Two layer region

$\%SnC1_2$	1.62	9.33	18.72	42.51	78.03	90.91
T.	243.1					243.1

(c) Solid phase $SnC1_2$

$\%SnC1_2$	94.71	97.88	100.0
T.	241.3	244.5	246.8

The curve shows one unstable compound of undetermined composition, which breaks up into a two liquid layer region extending over a range of ninety per cent, and which is here reported for the first time.

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[1] Lorenz and Eitel, Z.a.C., *91*, 61 (1915).

(23) SYSTEM $AlCl_3$-$SnCl_2$. See also curve F, Fig. II.

*(a) Solid phase Two layer compound $xSnCl_2,yAlCl_3$

$\%SnCl_2$	0.98	1.11	15.30	18.08
T.	191.0	191.3	191.0	188.2

(b) Two layer region

$\%SnCl_2$	2.01	8.76	13.68
T.	192.0		192.0

*(c) Solid phase $SnCl_2,2AlCl_3$

$\%SnCl_2$	22.08	28.46	30.70	33.50	38.78	43.12	47.06
T.	187.0	204.4	207.4	209.1	195.0	178.6	164.1
$\%SnCl_2$	48.47	53.90					
T.	158.7	136.9					

*(d) Solid phase $SnCl_2,AlCl_3$

$\%SnCl_2$	50.70	54.60	63.46	69.85
T.	158.2	153.3	142.3	135.4

(e) Solid phase $SnCl_2$

$\%SnCl_2$	68.52	70.95	74.96	86.09	90.85	100.0
T.	138.3	154.3	176.3	223.4	235.7	246.8

The curve shows two stable compounds with maxima at 209° and 158°.5 which have the composition $SnCl_2,2AlCl_3$ and $SnCl_2,AlCl_3$ respectively. There is also an unstable compound of undetermined composition which decomposes into two liquid layers. All three of these compounds are here reported for the first time.

(24) SYSTEM $SbCl_3$-$SnCl_4$. See also curve A, Fig. I.

The tin tetrachloride was prepared by the method of Erdmann,[1] by passing a stream of chlorine upon molten tin. By distilling from excess tin a colorless, chlorine-free product was obtained boiling at 114° and freezing at —30°.2.

T. C. indicates temperature of coalescence.

(a) Solid phase $SbCl_3$

$\%SnCl_4$		0.00	4.56	6.19	13.51	14.62	17.76	19.13
T.		73.4	70.9	69.4	67.7	67.4	67.0	66.8
$\%SnCl_2$		23.91	35.80	45.24	52.93	61.10	64.79	73.55
T.		66.5	66.3	66.1	66.0	65.9	65.8	64.6
T. C.		(?)	62.9	65.9	65.4	64.5	63.0	57.5
$\%SnCl_2$	83.00	92.06	94.64	95.62	98.08	98.71	99.43	99.66
T.	62.0	50.9	44.1	38.6	0.0	—10.6	—25.3	—30.0
T. C.	(?)							

The solid phase $SnCl_4$ could not be obtained except for the 100% tube, but from the slope of the curve it is evident that there is an eutectic. It is interesting to note that a metastable two layer region is present. The temperature of coalescence of the limiting tubes could not be obtained because solidification would occur.

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[1] Bender, Anleit z. Darst. anorg. chem. Präp., 1893.

(25) SYSTEM $AlCl_3$-$SnCl_4$.

(a) Solid phase $AlCl_3$

%$SnCl_4$	0.00	6.83	19.26	34.78	47.34	53.78	63.17
T.	190.2	188.6	182.6	174.2	167.8	164.5	158.3
%$SnCl_4$	74.41	83.40	89.58	93.20	95.93	98.84	99.65
T.	150.0	139.5	130.9	122.0	113.4	89.9	65.7

It was impracticable to carry the curve further, but from the slope it is probable that there is an eutectic.

(26) SYSTEM $AlCl_3$-$CrCl_3$.

Glistening purple, sublimed, C.P. crystals were used, but tubes containing 1% of the salt showed not the slightest signs of solution.

(27) SYSTEM $AlCl_3$-$CrCl_2$.

The C.P. anhydrous chromous chloride as supplied by the trade was green, so the sample was heated in a stream of hydrogen and hydrochloric acid. Only the white crystals were used, but during the filling and sealing of the tubes these were oxidized almost at once to chromic chloride and hence were insoluble as above.

(28) SYSTEM $AlCl_3$-$MnCl_2$.

C.P. manganous chloride was carefully fused in the presence of the least quantity of air possible and only the center portions of the fused mass were used.

(a) Solid phase $AlCl_3$

%$MnCl_2$	0.00	8.42	9.69	13.53	16.07
T.	190.2	190.0	189.9	186.4	185.4

*(b) Solid phase $MnCl_2,2AlCl_3$

%$MnCl_2$	19.14	20.93	23.53	31.42
T.	197.2	203.9	212.9	226.9

(c) Solid phase $MnCl_2$ (?)

%$MnCl_2$	32.41	34.91
T.	271.1	308.8

A tube containing 38% $MnCl_2$ would not give a clear solution at 370° for 6 hours; however, the curve is rapidly rising so that the solid phase separating is most probably manganous chloride. A new compound, $MnCl_2,2AlCl_3$, which is cut off at about 31.5%, is reported for the first time.

TABLE II

Halide	E.P.[2]	At. Diam.[1]	$SbCl_3$	$AlCl_3$	$AlBr_3$
Li+	3.02	3.0A	insoluble	1—1	1—7; 1—2; 1—1
NH_4+	(2.92)		1—1;3—2	*2 liq; 1—1	*2 liq; 1—3; 1—2; 1—1
K+	2.92	4.15	1—1;3—2	*2 liq; 1—1	*2 liq; 1—2; 1—1
Ba··	2.8	4.20	insoluble	* 1—2?	* 1—2?
Na+	2.72	3.55	insoluble	*2 liq; 1—1	*2 liq; 2—7; 1—2; 1—1
Ca··	2.5	3.40			*2 liq; 1—2?
Mg··	1.55	2.85		1—2?	1—2?
Al···	1.34	2.70	none		
Mn··	1.0	2.95		1—2	1—2
Zn··	0.76	2.65			1—2
Cr··	0.6	2.80		insoluble	
Cr···	0.5	2.80		insoluble	insoluble
Fe··	0.43	2.80			1—2
Cd··	0.4	3.20			1—2
Tl+	0.33	4.50		*2 liq; 1—2; 1—1	*2 liq; 1—2; 1—1
Ni··	0.22	2.70			insoluble
Pb··	0.13	3.80			* 1—2
Sn··	0.10	2.80	*2 liq	*2 liq; 1—2; 1—1	* 1—2; 1—1
Sn····	0.05	2.80	*none	none	none
Sb···	0.1	2.80		none	1—1
Bi···	0.2	2.96			1—1
As···	0.3	2.52			none
Cu+	0.52	2.75	insoluble	1—1	
Hg+	0.79		insoluble	* abandoned	* 1—1
Ag+	0.8	3.55	insoluble	*2 liq 1—1	* 1—2; 1—1
Hg··	0.86		none	none	1—2

DISCUSSION OF RESULTS

The above results are given in Table II. A list of the halides studied is presented in Column 1. In Column 2 is found the electrode potential. The atomic diameters in Angström units of the positive radicals are given in Column 3. In the remaining columns are shown the compounds formed between $SbCl_3$,$AlCl_3$ and $AlBr_3$ with the proper halide of the element in Column 1. The figures refer, as in Table 1, to the molecular composition of the compound—the latter figure representing the amount of solvent. Systems showing immiscibility are starred, while "2 liq" indicates an unstable compound of undetermined composition which breaks down into two liquid layers.

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[1] Bragg, Phil. Mag. (6) *40*, 169 (1920).

[2] Abegg, Auerbach and Luther, Abhandl. Deutsch. Bunsen Ges., 2 No. 5, 1911; No. 8, 1915, together with several minor changes due to Lewis et al, J.A.C.S. *36*. 804 (1914); *37*. 1990 (1915); *39*. 1912 (1917); Linhart, ibid., *88*. 2356 (1916); Heyrovsky, J. Chem. Soc. *117*. 27 (1920).

As one examines Table II above and compares the compounds formed with $SbCl_3$,$AlCl_3$ and $AlBr_3$ one is struck by the fact that the compound formation increases in that order, and particularly that antimony trichloride is such a poor solvent. That antimony is below hydrogen in the E.M.F. series may account for the insolubility of the chlorides of the electro negative elements,—antimony and silver being only 0.7 of a volt apart,—but hardly for the indifference of lithium, sodium and barium chlorides. The antimony salt has a lower melting point and is unsaturated, both of which characteristics would tend to make it a better solvent than aluminium chloride. The aluminium chloride has a slightly less internal pressure and a somewhat smaller atomic diameter, though these factors would scarcely account for the striking difference in behavior. Association, ionization and heat of fusion are probably of the same order, and it is evident that some other factor must be exerting an influence. Discussion of this point will be taken up in a later paragraph.

Aluminium chloride is seen to be not as good a solvent as aluminium bromide, but here the variance[1] in temperature of their respective melting points is sufficient to explain the difference in behavior. Aluminium bromide shows all the compounds of aluminium chloride and many additional ones, which are either so unstable, or their maxima are at such low temperatures, that they are decomposed at the higher temperatures necessary for solution in aluminium chloride. Further discussion of this temperature effect may be had from earlier papers of this series already referred to, and the excellent article by Sir J. J. Thomson.[2]

The compounds with the same solvent beautifully follow the rules already laid down in previous articles of this series. The alkali halides form numerous compounds, as many as four different ones being isolable in the cases of ammonium and sodium bromides. Twenty-five compounds were isolated in the ten systems of alkali halides which gave solubility curves. The halides of the alkaline earth metals give usually one compound while the salts of chromium, nickel and stannic tin give none. With the salts of copper, mercury and silver we again notice an increase in the number of compounds formed. The exceptions will be discussed below, but it is evident that as our reference element is approached from both ends of the electro motive series the compound formation becomes less, and that the greater the diversity the greater is the tendency toward compound formation. Though the paucity of compounds in comparison with previous work where hydrogen is the reference element, is evident, it can be explained by the valence factor.

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[1] It will be noted that $AlBr_3$ melts at 97°.1 while the melting point of $AlCl_3$ is almost a hundred degrees higher, 190°.2.

[2] Phil. Mag., *27,* 757 (1914).

VALENCE FACTOR.

It will be noticed, in general, that the lower the valence the greater will be the compound formation and the greater the solubility. This is very evident from an examination of the systems run previously in this series, and from a glance at the tables of solubilities given in those papers. For example, in the solubilities of the metal hydroxides in water; aluminium and ferric hydroxides are practically insoluble, the divalent hydroxides are more soluble and the univalent are very soluble. Many of the exceptions previously noted, as for example that sodium formate is more soluble than the barium salt in formic acid; that sodium sulphate is more soluble than barium sulphate in sulphuric acid, while aluminium sulphate is practically insoluble, may be explained by this valence factor. Similarly in the present comparisons sodium is more soluble than barium chloride, and silver and copper (ous) than mercuric chloride. Thallous chloride, even taking into account this valence factor seems to be very much more reactive than its position in the E.M.F. series would indicate. This is very probably due in large part to unsaturation.

UNSATURATION.

If we examine the available data on the solubility of compounds RXm and RXn in HX (R being a metal which has two different valences) we find in every case that the compound in which the metal has the lower valence shows the greater solubility. To give but a few examples; in water, ferrous hydroxide is more soluble than ferric, as also thallous is more soluble than thallic hydroxide; in sulphuric acid, ferrous sulphate is more soluble than ferric, and mercurous than mercuric. Throughout this series the sulphate, formate and hydroxide of plumbous lead are all soluble to a degree unexpectedly great from the position of lead in the E.M.F. series, due probably to this unsaturation effect. We can best account for this by assuming that the compound containing the metal in the lower state of oxidation has the greater tendency toward compound formation. If we consider these compounds from Werner's point of view,[1] regarding the metal as the central atom, this hypothesis is in harmony with the theory of coordination number. Again in the present work unsaturation presumably accounts for the large number of compounds with stannous chloride and for the fact that manganous chloride gives a compound with aluminium chloride although manganese is next to aluminium in the electromotive series.

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[1] New Ideas on Inorganic Chemistry, pp. 47-54.

TABLE III

INTERNAL PRESSURES

$$II = 20.65\ (5200+30t_b)/V_{20}$$

$SnCl_4$	1,550
$SbCl_3$	3,318
$AlCl_3$	3,897
$BiCl_3$	5,460
$HgCl_2$	5,905
HgCl	10,374
$ZnCl_2$	11,910
TlCl	16,228
KCl	26,270
CuCl	27,145
AgCl	28,200
NaCl	37,150
LiCl	44,810

II = pressure in atmospheres

t_b = centigrade temperature of boiling

V_{20} = molecular volume at 20°C.

INTERNAL PRESSURE.

With the chlorides as with the bromides[1] a large number of two liquid layer systems have been noted, arising for the most part from the breaking up of an unstable compound of undetermined composition. Here also the salts of potassium and ammonium behave similarly in respect to forming immiscible systems. Using a formula[2] suggested by Hildebrand[3] to calculate internal pressure (see Table III) the same results are found as with the bromides[4]; that two layer systems are found where there exists a large difference in internal pressures. Sodium, silver, potassium and thallous chlorides all give a region of immiscibility with aluminium chloride. Cuprous and lithum chlorides would be expected to give two layer systems, but similarly to lithium bromide we observe merely a tendency to form two layers manifest by a flattening of the curve. The data for calculating the internal pressure of stannous chloride were not available, although it is doubtful if it would be over 7000 atmospheres, which pressure would hardly account for the two layers observed. Stannic chloride and antimony trichloride show decided indications of a metastable region of immiscibility though no such region is noted with aluminium chloride. Potassium chloride fails to show even a flattening of the curve with antimony trichloride. However, the work of Hildebrand is still in the experimental stages and in the near future it is hoped that an explanation will be had which will account for the above anomalies. In the meanwhile attention is called to the discussion of two liquid layer systems given by Crittenden.[1]

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[1] Crittenden, loc. cit.

[2] Based on Stefan's assumption.

[3] J.A.C.S., *41* 1068 (1919).

[4] Crittenden, loc. cit.

IONIC DIAMETERS.

In connection with these two layer systems it is of interest to interpret the results here obtained by the purely physical theory of Holmes.[2] He assumes the absence of chemical change and then shows that any two liquids, the molecular spheres of which have equal radii, should be miscible in all proportions. If however the radii are of different sizes there should be immiscibilty between the ratio of 1.618 to 1 and 2.414 to 1. By using the atomic diameters[3] given by Bragg[1] and assuming with him that molecular diameters are additive[4] we should be able to compare roughly molecular radii.

Aluminium has an atomic diameter of 2.7 Angström units. With the chlorides and bromides here investigated we observe two layers with K, Ba, Na, Ca, T1, Pb and Ag, all of which have atomic diameters greater than 3.5 and less than 4.5. Of the elements with diameters close to 3, lithium, cadmium and manganous manganese as chlorides show indications of a tendency toward two layers, although Bi, 2.96 does not. Stannic tin, 2.80 shows no signs of two layers, as would be expected, but with stannous tin we have an exception for it gives immiscibility with all three of the solvents tried. Antimony trichloride throughout acts exceptionally, since even the higher valent tin gives a metastable region of immiscibility and potassium chloride shows no signs whatsoever of two layers, although potassium has a diameter of 4.15. It is evident that the theory holds as well as that of internal pressures at the present stage of development but as was stated above we must still wait for an explanation satisfactory in all cases.

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[1] Loc. cit.

[2] J. C. S. 103 (1913) 2147.

[3] See Table II.

[4] The molecular volume of a compound is in general very far from being equal to the sum of the molecular volumes of the elements comprising it. However, if the distances between the atoms are taken as a measure of the space they occupy, Bragg has found that an additive law holds with considerable accuracy.

INSTABILITY FACTOR.

It remains to discuss the anomalous behavior[1] of $SbCl_3$ and the instability of its compounds in comparison with $AlCl_3$ and $AlBr_3$. If we examine the simple metallic chlorides, we see that those of the alkalis are very stable; as we descend the E.M.F. series they become less and less stable until we reach the chlorides of silver and gold, which are decomposed by slight shock, as light or gentle heat. Antimony chloride being the compound of a metal low in the list, is therefore much more unstable than $AlCl_3$ the positive radical of which is much above hydrogen. Now the compounds which each of these salts form with other chlorides will of necessity be more unstable than the simple chlorides themselves in view of the greater complexity of the molecule. Consequently it is quite possible that while antimony trichloride has a great tendency to form compounds with other chlorides, these compounds are so unstable that they are decomposed at the temperature of the fused salt mixture and we have very few compounds actually isolable. This point will be examined in greater detail in later work, in connection with systems containing varying negative radicals.

DISCUSSION OF PREVIOUS WORK.

If we now turn back to Table 1, of compounds reported in the literature, we can explain the seeming exceptions and discuss the entire field of fused chlorides. There are no compounds of trivalent chlorides with chlorides of the same or higher valence; no trivalent with divalent save the ones discussed above in this research; and of trivalent with univalent besides those of the present work, only ferric chloride with ammonium and with cuprous chlorides. In both cases equimolecular compounds are reported. Cuprous copper is unsaturated, which fact increases the tendency of its salts to form compounds, while throughout, ammonium salts manifest a great tendency, at present unexplained, toward compound formation. Of the didivalent systems we find only the compounds $2BaCl_2,MnCl_2$; $BaCl_2, ZnCl_2$; $ZnCl_2,SrCl_2$. The manganese is unsaturated and so would tend to greater compound formation, as would barium because of the diversity factor, being itself much more electro-positive than manganese or zinc. The zinc has an unusually small atomic volume and so as shown previously tends to form more compounds than otherwise. With the uniunivalent systems of the electropositive elements we have only the compounds CsCl,LiCl and 2CsCl,LiCl, which can be explained as above, as due to the small atomic volume of lithium; of the electronegative elements no compounds are reported. Cuprous and silver chloride give compounds with the chlorides of caesium and thallium, and cuprous also with lithium, rhubidium and potassium chlorides. Here we have the extreme diversity factor coupled with the unsaturation of copper and thallium. There are twenty-three compounds of the unidivalent type reported which with the twenty-four compounds reported in this research gives striking evidence that diversity of valence of the positive radical is also a factor to be taken into account in predicting compound formation. The above brief discussion shows very plainly what important parts valence and unsaturation play in compound formation in fused salt mixtures.

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[1] See page 25.

Many attempts[1] have been made to explain compound formation among the halides by means of valence, and many workers have compiled tables of the compounds reported with salts of different valences, but no satisfactory conclusions have been drawn. In this consideration it is interesting, however, to note that with a trivalent salt as solvent it has been found, with the chlorides and bromides here studied, that monovalent salts give a stable equimolecular compound and divalent salts one in which the proportion of solvent is twice that of the solute. Numerous other compounds are no doubt formed and some of these are isolable but they are not as stable as those of the above proportions.

The systems $ZnCl_2$-$BiCl_3$ and $ZnCl_2$-$HgCl_2$ give the only two liquid layer regions previously reported in binary chloride systems and can be explained as above by the difference in internal pressures or by atomic diameters.

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[1] Note particularly, Wells, loc. cit.; Remsen, Am. Chem. J. 11, 316 ibid *14*, 81 (1892).

SUMMARY

In the foregoing discussion it has been shown that in systems of fused chlorides the rule previously expounded in this series is followed;—that compound formation increases with increase in chemical diversity, as measured by the difference in electrical potential when compared against hydrogen ion. This is the main factor in compound formation, but additional factors influencing the extent and stability of the compounds formed have here been pointed out and examined.

Comparisons have been made between $SbCl_3$,$AlCl_3$ and $AlBr_3$ as solvents, and the compounds formed.

It has been shown that of the additional factors, the greatest influences are exerted by valence and unsaturation.

To a less extent the influence of internal pressure, atomic diameters, and temperature of fusion have been discussed.

Twenty-eight new systems have been investigated.

Seventeen compounds have been isolated for the first time.

During the course of the investigation it has been shown that antimony trichloride exists in three crystalline modifications.

VITA

Henry Keppele Miller, junior, was born in Wilmington, Delaware, on February 15, 1899, and attended the Friends School of that city. He received the degree of B.S. from Princeton University in 1920 From that time to the present he has attended the graduate school of Columbia University, and taught in the Department of Chemistry. He received the degree of M.A. from Columbia University in 1921. During the college year 1921-22 he also taught in the College of the City of New York. He is a member of Phi Beta Kappa, Phi Lambda Upsilon, and Sigma Xi.

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